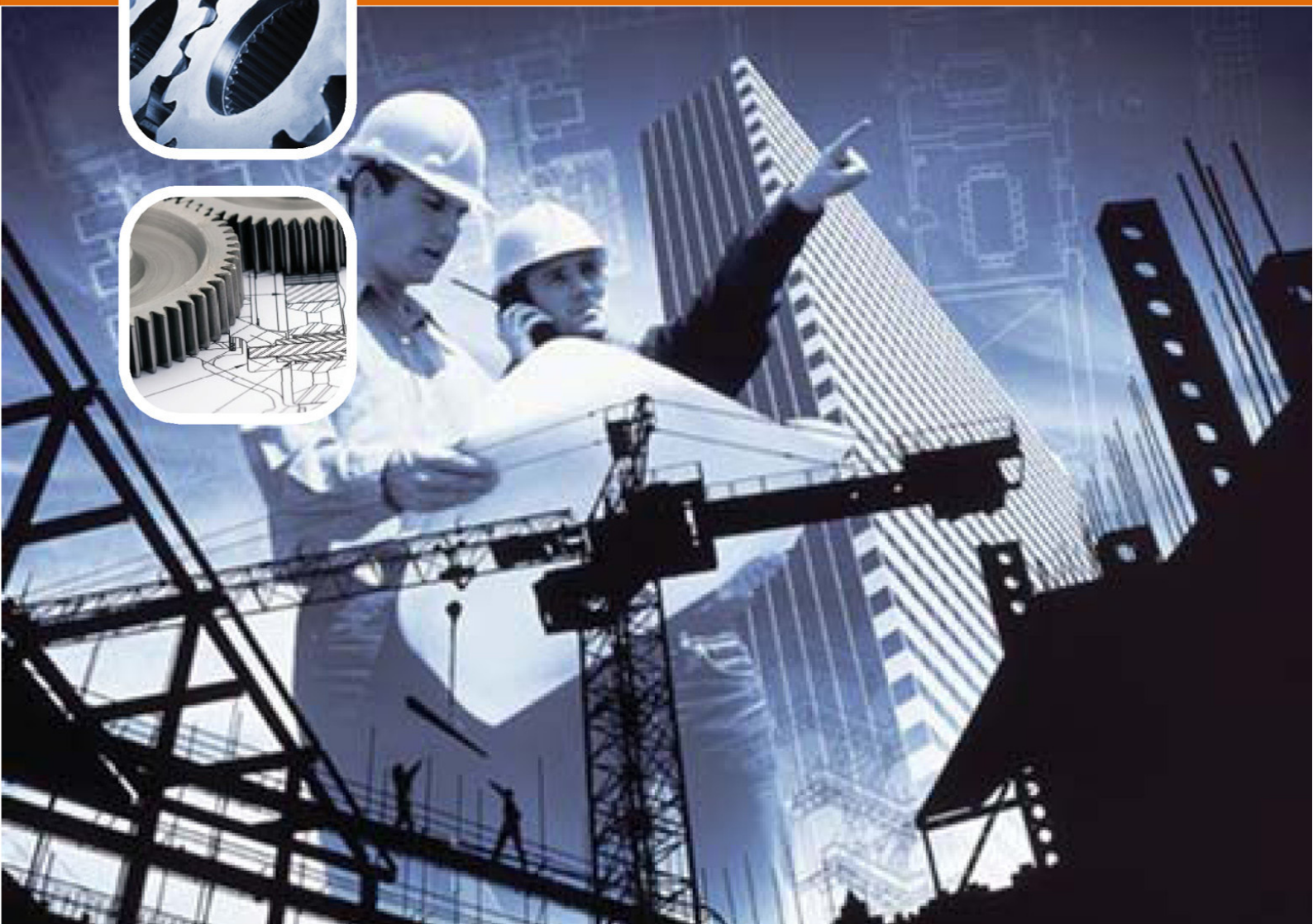


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CONTINUOUS BIODIESEL PRODUCTION WITH ANION-EXCHANGE RESIN

Takuya Ito¹, Yusuke Kakuta², Katsumi Hirano³, Hideki Suganuma⁴, Shigeru Kato⁵, Seiichi Suzuki⁶ and Toshinori Kojima⁷

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ABSTRACT

Biodiesel attracts attention as an alternative to fossil fuel. Though the raw material of biodiesel is renewable and carbon neutral, in the conventional method the product is contaminated with the homogeneous alkali catalyst. Hence, the application of the anion-exchange resin was used as the solid base catalyst. While the method of using the anion-exchange resin has already been reported, a problem in durability remains. In the present paper, the reaction mechanism of the transesterification using the anion-exchange resin was examined. As a result, it was suggested that the ion exchange between the hydroxyl ion of the resin and the methoxide ion of the methanol occurred first in the transesterification when the anion-exchange resin was used. The fatty acid was generated by hydrolysis of triglyceride because the water was generated along with this ion exchange reaction. Then, the methoxide type anion-exchange resin without hydroxyl group was made as starting material for experiments. The applicability of the methoxide type anion-exchange resin to the fixed bed reactor in the biodiesel manufacturing process was examined. As a result, its applicability was confirmed by using a part of producing biodiesel as the recycling solvent and by adding excessive methanol.

Keywords: biodiesel; anion-exchange resin; transesterification; methoxide ion; fixed-bed reactor.

1. INTRODUCTION

The world petroleum supply in 2012 was 89.7 million barrels/day as it fulfilled about 33% of the world's primary energy demand. The world demand is predicted to reach 95.7 million barrels/day by 2017. This increase is 7% of 2012 levels which was 5 million barrels/day. The increase in demand is centering in China and Asia. Meanwhile, the reserves-to-production ratio is about 59 years (Petroleum Association of Japan Petroleum Industry, 2013).

Biodiesel is attracting attention as one of the possible alternative fuels to petroleum. Basically, biodiesel is comprised of fatty acid methyl esters (FAMES), which are produced by the transesterification of triacylglycerols (TGs), the main component of fats and oils, with methanol and homogeneous alkali catalysts (Ex. NaOH, KOH, ect.). Biodiesel can be used in existing diesel engines, and as it vanishingly contains sulfur, SO_x is hardly emitted. In addition, the flash point of biodiesel is high and complete combustion can be achieved, with

reduced emissions of HC, CO, and black smoke. However, the use of the homogeneous alkali catalysts cause the production of the harmful alkaline waste fluids in the water washing process (Saka, 2010).

The method of using a variety of solid base catalysts to avoid this problem is reported (Liu & Zhang, 2011; Endalew, Kiros & Zanzi, 2011; Liu, Su, Liu, Li, & Solomon, 2011). Though the metal oxide catalyst is reported to show very high activity, its dissolution problem into the biodiesel is unsettled (Kozu et al., 2008).

Hence, the attention was paid to ion exchange resin method. This method uses the anion exchange resin instead of the homogeneous alkali catalysts. As a result, the continuous processes with fixed-bed reactors can be constructed without the water washing process involve the production of the harmful alkaline waste fluids. However, the regeneration process of the frequent anion exchange resin is necessary, because of this poor durability (Shibasaki-Kitakawa et al., 2007).

Authors have reported on a device approach so far (Ito, Kakuta, Hirano & Kojima, 2014). In the present study, the transesterification mechanism with the anion exchange resin and the change of the catalytic property was examined. As a result, a new preparation method of the anion exchange resin with improved durability was proposed. Moreover, the durability of the improved anion exchange resin was examined with the fixed-bed reactor.

2. METHODOLOGY

2.1 Catalyst preparation

Anion exchange resin (Organo Corporation, IRA204Cl) of 400 mL was swelled in methanol and the column equipped with glass filter was filled with it. The sodium hydroxide solution (1 mol/L) or sodium methylate-methanol solution (1mol/L) of 4 L was poured into the column at the speed of space velocity (SV) = 4h^{-1} . Next, pure water or methanol of 8L was poured into it at SV = 10h^{-1} . Methanol of 500ml was poured into it under pressurizing. The resin made by using the sodium hydroxide was assumed to be OH type and the resin made by using the sodium methoxide was assumed to be CH₃O type. Table 1 lists the properties of the anion exchange resin used.

2.2 Transesterification (batch reactor)

A thermometer, a nitrogen supply nozzle, and a Dimroth condenser were installed in a three neck Erlenmeyer flask (300 mL capacity). The soybean oil (100 g), the methanol or methanol-d₄ (60 wt% - soybean oil basis), and OH or CH₃O type resin (40 wt% - soybean oil basis) were put in the flask. The flask was kept warm at 65°C and liquor in the feedstock tank was stirred with a hot plate stirrer. The nitrogen of 40mL/min was supplied to the flask throughout the reaction experiment of 1-6 hours. Then, liquor in the flask was filtered and the methanol was removed from it with a rotary evaporator. The obtained liquor was analyzed by ¹H-NMR to get FAME amount (Neto, Caro, Mazzuco & Nascimento, 2004).

2.3 Transesterification (fixed-bed reactor)

The transesterification process flow using the fixed bed reactor is shown in Figure 1. The reaction tube (Length/diameter ratio (L/D) = 5, capacity of 400 ml) was filled with the CH₃O

type resin. A thermocouple, a nitrogen supply nozzle, and a Dimroth condenser were installed in the feedstock tank (2 L capacity). Soybean oil, methanol (30, 60 and 90 wt% - soybean oil basis), and the methyl oleate (100, 150 and 200 wt% - soybean oil basis) were put in the feedstock tank. The methyl oleate was used because it is one of the main components of FAME while, in the actual operation, mixed FAME will be used. Soybean oil and Methanol were used as feedstocks and the methyl oleate as a homogenizing solvent. The feedstock tank was kept warm at 50°C with an immersed heater. Liquor in the feedstock tank was stirred by a magnetic stirrer. The liquid in the feedstock tank was sent to from the bottom of the reaction tube with a tube pump at the rate of 0.5, 1.0, 2.0 ml/min to an eggplant flask as the product from the top and the flask was replaced with a fresh one every hour. The continuous operation was done for 30 h. The sample in the flask was post processed as well as the case of the batch reactor. The inner reaction tube was equipped with the outer tube in which the warm water in the water bath was circulated with using a pump to keep the inner tube temperature at 50°C.

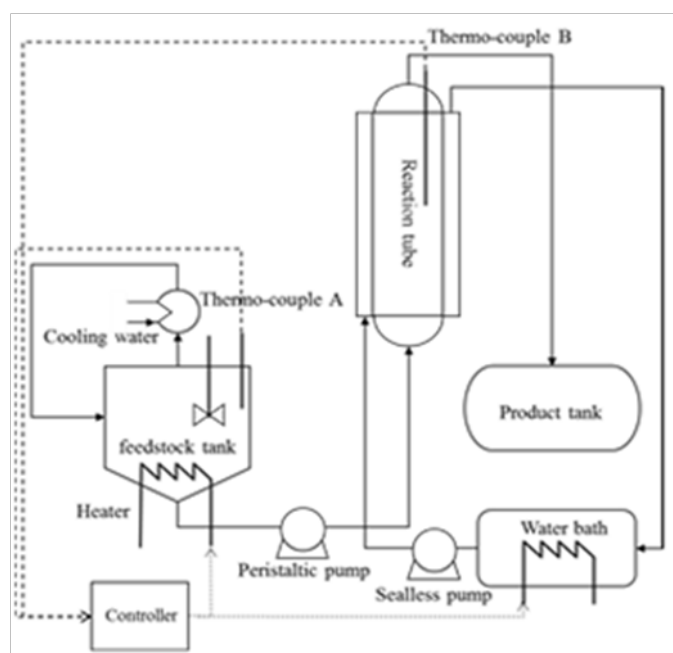


Figure 1: The process flow of the fixed bed reactor used.

3. RESULTS AND DISCUSSION

3.1 Reaction mechanism

Figure 2 shows the change of the FAME conversion when the OH type resin was repeatedly used in the batch type reactor. The reaction rates of the 2nd and 3rd use were higher than that of the virgin use. The following reaction mechanism (Figure 3) shows this result. First of all, the hydroxyl ion originally in the fresh anion exchange resin proposed based on is replaced on the methoxide ion by methanol. FAME is generated as this methoxide ion reacts with TG. The diacyl glyceride is generated with FAME unites with the ion exchange resin instead of the methoxide ion. However, this diacyl glyceride is replaced on the methoxide ion of another methanol. Afterwards, it is thought that the methoxide ion is repeatedly adsorbed and desorbed with the ion exchange group and this mechanism is repeated. In other words, it is thought that the methoxide ion adsorbed by the ion exchange group is an active species in the transesterification process using the anion exchange resin. Therefore, the 2nd time reaction

rate was increased because the methoxide ion has been adsorbed on the ion exchange resin by the 1st reaction.

Table 1: Properties of the anion exchange resin used.

Amberlite	IRA904 Cl
Character	Anion
Group	$-N \equiv (CH_3)_3X$
Type	macro reticular
Ion-exchange capacity[mol/g-resin]	≥ 4.2
Surface area[m ² /g-resin]	46.9
Particle size[mm]	0.4-0.56

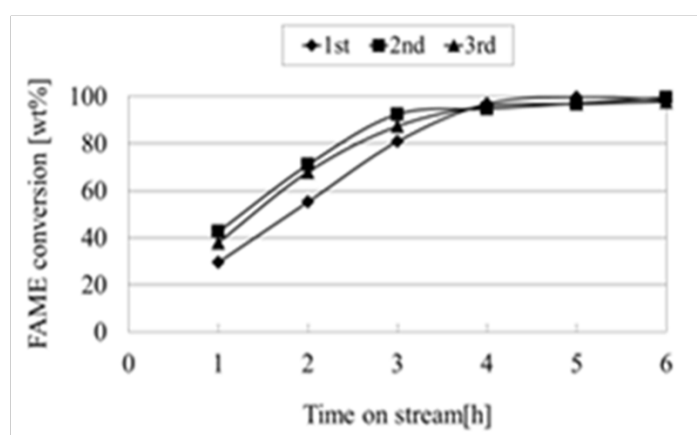


Figure 2: The change of the FAME conversion when the OH type resin is repeatedly used in the batch type reactor.

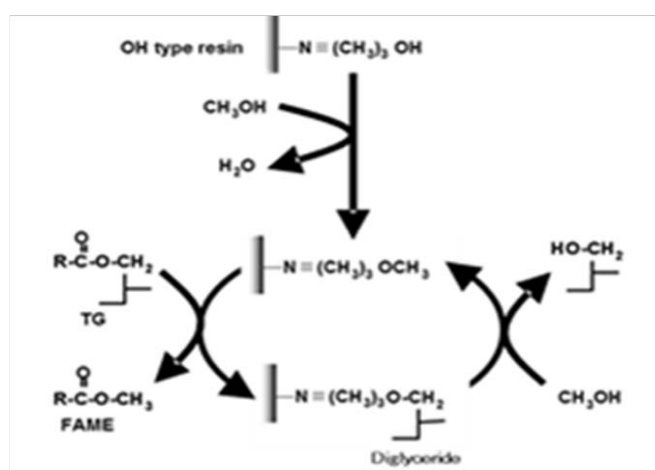


Figure 3 : The conceptual mechanism intranesterification using anion-exchange resin.

To confirm this reaction mechanism, the tracer experiment using the methanol-d₄ was carried out and the result was compared with that of normal methanol. The mass spectrum of the methyl palmitate obtained when methanol-d₄ is used for the 1st reaction and the normal methanol is used for the 2nd reaction is shown in Figure 4. The mass spectrum of the normal

methyl palmitate is shown in Figure 5. As shown in Figure 4, m/z 77 and 90, in addition to m/z 74 and 87, characteristic fragment-ions of FAME were detected (Ogawa, 1996). As shown in Figure 5, m/z 77 and 90 fragment-ions are not detected in a usual palmitic acid. It is presumed that m/z 77 and 90 fragment-ions are fragment-ions of the FAME-d3 originally from the deuterium in the methyl group of FAME (Sakia & Walter, 2006). Thus, it was thought that the methoxide ion of methanol-d4 origin was adsorbed by the fresh ion exchange group, and then this is carried over to the second reaction and FAME-d3 was generated. Therefore, it was confirmed that the transesterification using the anion exchange resin occurs after the methoxide ion adsorbs on the ion exchange resin.

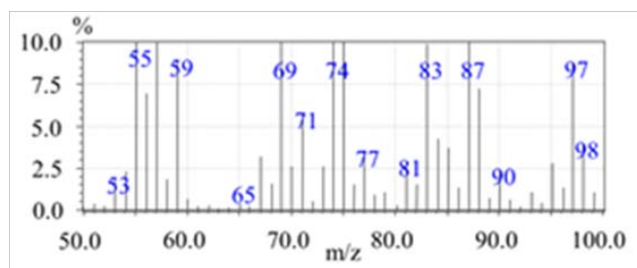


Figure 4 : The mass spectrum of the methyl palmitate obtained by 2nd reaction using normal methanol after 1st reaction using methanol-d4.

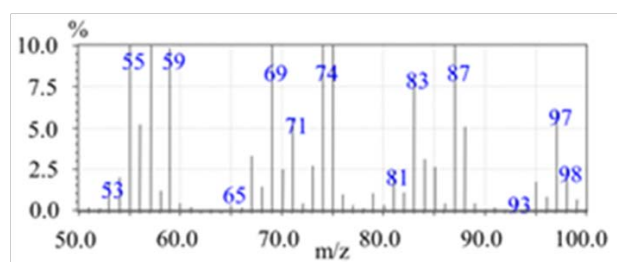


Figure 5: The mass spectrum of the normal methyl palmitate.

3.2 Deactivation mechanism

FT-IR spectra of OH type spent resin and original resin were shown in Figure 6. As shown in Figure 6, the peak of carboxylic acid salt ($1610\text{--}1550$ and $1420\text{--}1300\text{ cm}^{-1}$) unfound in the original resin exists in the spent resin. The carboxylic acid adsorbed on the resin was thought to be fatty acid generated with the ester hydrolysis reaction of TG with the hydroxyl ion as shown in Figure 7 (Xuejun, 2008). Therefore, it was clarified that we have to select the catalyst without the hydroxyl ion. The IR-spectra of CH_3O type original resin and spent resin were shown in Figure 8. As shown in Figure 8, the spectrum of the spent resin is almost the same as the original resin. Therefore, the CH_3O type resin has the possibility of high durability.

3.3 Durability

The effect of methanol on transesterification reaction with CH_3O type resin by fixed-bed reactor is shown in Figure 9. As shown in Figure 9, the FAME conversion began to decrease at 10 h and kept decreasing when the methanol was added by 30 wt% -soybean oil basis. Meanwhile, when the added amount of the methanol was increased, the FAME conversion became constant after decrease. It is possible that the resin is deactivated because

monoglyceride and diglyceride are adsorbed on the ion exchange resin, which is not replaced with methanol with less concentration of 30 wt%. However, when 60wt% or more puts the methanol, it is thought that the ion exchange is promoted and the deactivation of the resin was inhibited.

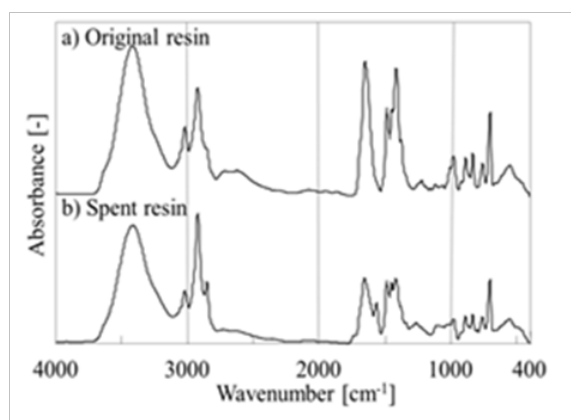


Figure 6: FT-IR spectra of OH type spent resin and original resin.

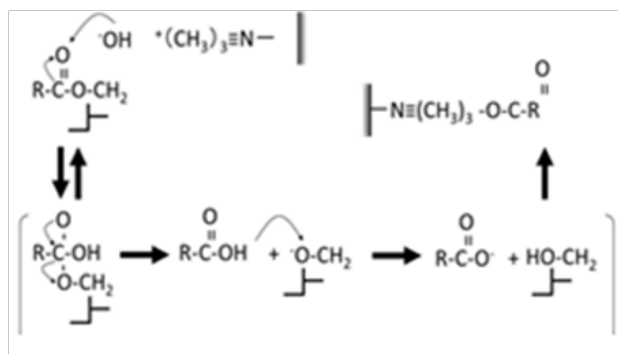


Figure 7: Deactivation mechanism of OH type resin.

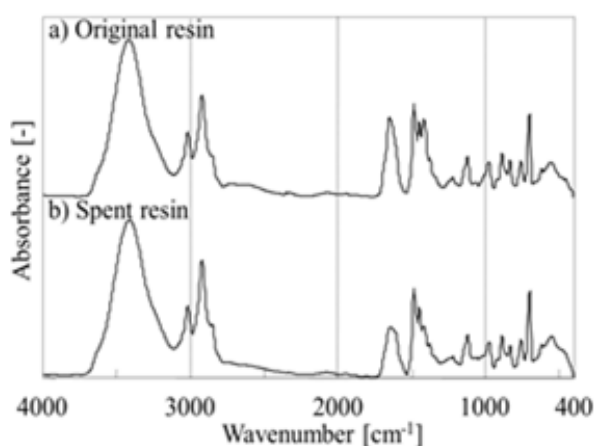


Figure 8: The IR spectra of CH₃O type original resin and spent resin.

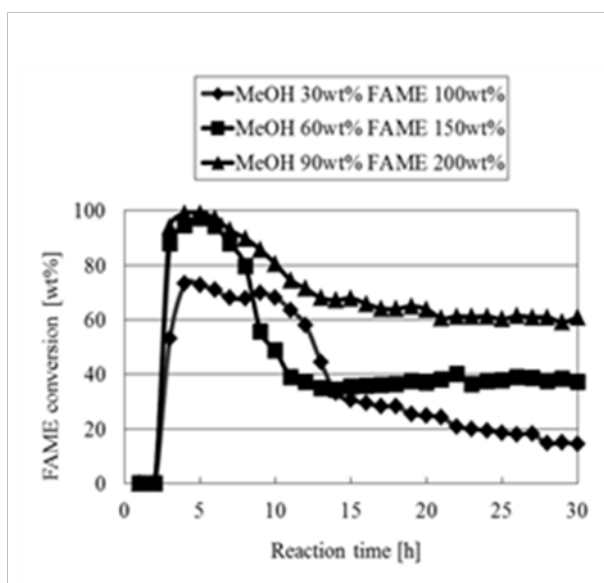


Figure 9: Effect of methanol on transesterification reaction with CH_3O type resin by fixed-bed reactor.

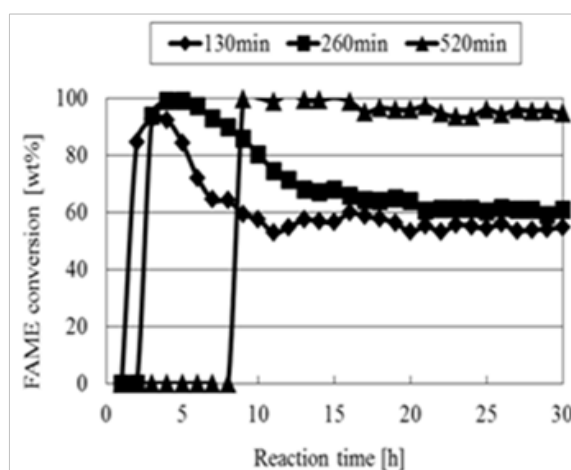


Figure 10: Effect of residence time (flow rate) on time variation of transesterification reaction with CH_3O type resin in fixed-bed reactor.

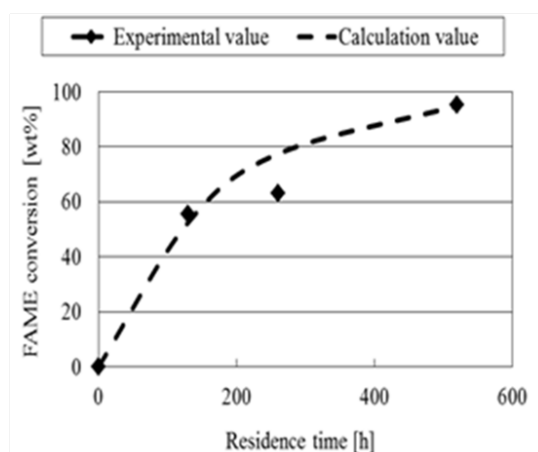


Figure 11: Comparison between calculated by kinetic analysis and experimental steady state FAME conversion values.

3.4 Rate-determining step

The effect of residence time, namely flow rate on transesterification reaction with CH₃O type resin in fixed-bed reactor was shown in Figure 10. Comparison between calculated value assuming the first order kinetics and experimental steady state value of FAME conversion was shown in Figure 11. As shown in Figure 11, when the residence time is adjusted to 520 min, the FAME conversion reaches about 95wt%. The calculated value and the experimental value show a good agreement. Thus, because the calculation value is influenced only by the simple first order kinetics, it is thought that the influence of the other physical factors such as the influence of flow refine on adsorption and desorption is not large and this reaction rate is controlled by the surface reaction rate.

4. CONCLUSION

The tracer experiment showed that the transesterification using the anion exchange resin occurs after the methoxide ion adsorption on the resin. Because the CH₃O type resin does not generate the fatty acid while reacting, durability is high. Catalytic activity of CH₃O type resin decreases gradually if it drives continuously. However, catalytic activity can be kept constant by increasing the amount of the methanol addition and promoting the ion exchange. This reaction is a surface reaction rate-determining. The prospect of high biodiesel yield was demonstrated able to be manufactured from high yield obtained from durable methoxide type anion exchange resin in a fixed-bed reactor.

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